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Microwave Treatment of Oxidizer Vapor

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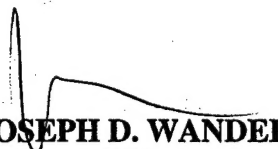
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Paper

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ABSTRACT

During fueling of liquid rockets, transfer of the propellant, hydrazine (and its monomethyl and 1,2-dimethyl derivatives), and of the oxidizer, dinitrogen tetroxide (N_2O_4) creates exhaust streams of nitrogen gas heavily contaminated with these constituents. Wet scrubbers provide ~60% removal of these contaminants, and combustion devices emit unacceptable amounts of NO_x as byproducts of treatment. The Air Force Research Laboratory, Weapon Systems Logistics Branch (AFRL/MLQL) has developed a systematic assessment of needs for pollution prevention research within the space segment of Air Force activities. The MLQL team has identified development of a Toxic Propellant Vapor Treatment process to improve on current scrubber technology for treatment of this exhaust as one of two specific, high-priority needs of common concern to several locations.

Toward that goal, CHA Corporation is conducting a staged development effort leading to a field demonstration of a full-scale microwave reactor system to decompose both N_2O_4 vapors and hydrazine vapors in [separate] nitrogen gas streams. We expect to carry the development through to deployment as an operational technology.

During phase 1, we completed design optimization experiments and assembled a 5–10-scfm prototype reactor system. Efficient reduction of NO_x formed by dissociation of N_2O_4 is realized by passage through a bed of carbon during microwave irradiation. To extend the lifetime of the carbon bed, which is consumed as a reductant in this process, we introduced a slight stoichiometric excess of alcohol upstream of the bed. This approach achieves consistent 99+% reduction of net NO_x species over a range of irradiation power levels and residence times.

Considerations in the design of a 50–100-scfm pilot-scale reactor will also be discussed.

INTRODUCTION

The Air Force Research Laboratory, Materials and Manufacturing Directorate (AFRL/ML), has developed a systematic approach for identifying needs for pollution prevention research with the space segment of Air Force activities. This team has canvassed many USAF and NASA organizations, and determined that two specific needs are of common concern to several locations and hence have high priority. One of these is development of a Toxic Propellant Vapor Treatment process.

During fueling or defueling of liquid rockets, transfer of the propellant, hydrazine (and/or 1-methylhydrazine [MMH] or 1,2-dimethylhydrazine [UDMH]), and of the oxidizer, dinitrogen tetroxide (N_2O_4), is driven by nitrogen gas pressure. Displacement of the contents of headspaces to accomplish transfer of the fuel or oxidizer creates exhaust streams of nitrogen gas heavily contaminated with these very toxic constituents, which are regulated as air pollutants.

Emission control by passage through wet caustic scrubbers may approach the predicted^{1,2} limit of 66% removal of these contaminants, and prototype combustion devices that were tested as alternative control methods consumed large quantities of natural gas and achieved only fair net reduction of NOx. During a Small Business Innovation Research (SBIR) investigation sponsored by AFRL/MLQL, CHA Corporation (CHA) demonstrated³ efficient reduction of nitrogen dioxide (NO_2) but not of nitric oxide (NO) by passing diesel combustion exhausts through a bed of activated carbon irradiated with ~1 kW of microwave power.

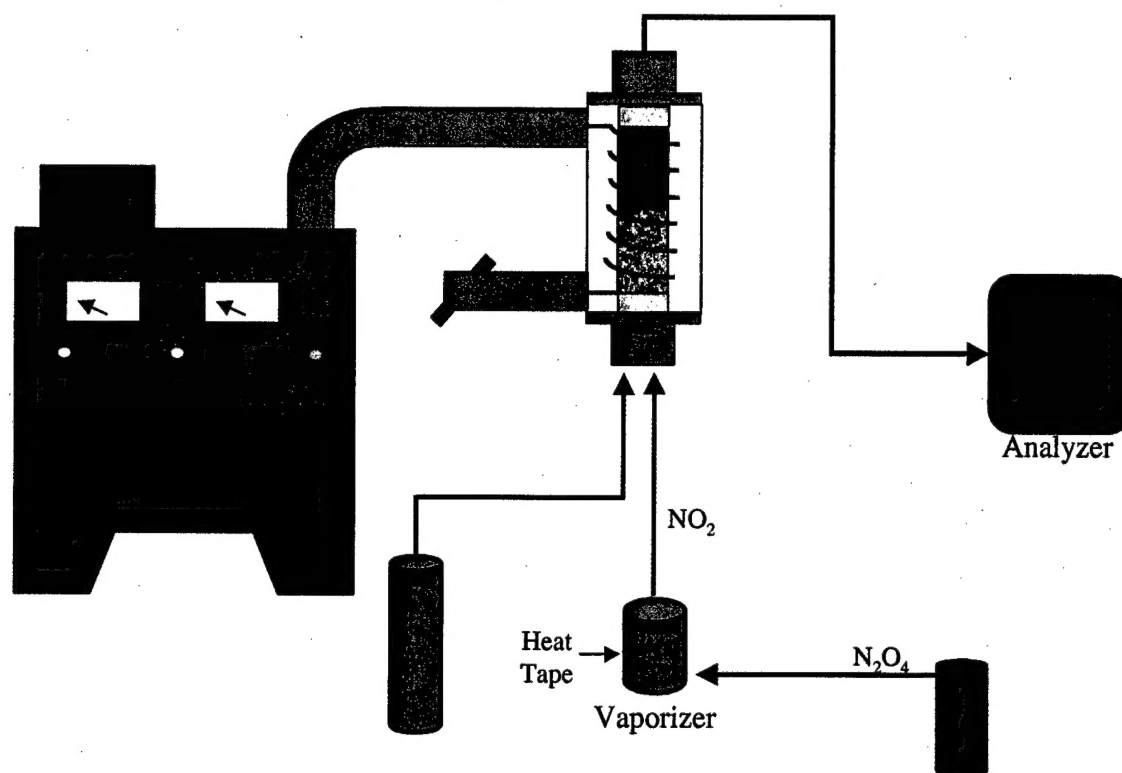
Investigations of different methods of NOx reduction have consistently shown⁴⁻⁶ that the slow step is oxidation of NO, which is almost completely inert to reduction and practically insoluble in water, to NO_2 , which is readily reduced by a variety of reagents and catalysts, and slightly soluble in water. CHA's phase II SBIR project recognized that N_2O_4 is a dimer that dissociates to form NO_2 in the gas phase, and the feasibility of applying microwave methods to decompose hydrazines as well was explored briefly at the end of that contract. In addition to improving efficiency of control, the microwave destruction method uses no caustic solutions and would, therefore, also greatly decrease the cost to control emissions from fuel- and oxidizer-transfer operations.

This project is phase one of a two-phase program to conduct a field demonstration of a microwave reactor system to decompose both nitrogen tetroxide (N_2O_4) vapors and hydrazine fuel vapors in a nitrogen gas stream. The program's goal is to advance the development to a point that it can be deployed as an operational technology to NASA and Air Force space operations. This paper presents results from a series of design optimization experiments for the destruction of nitrogen tetroxide vapor.

DESCRIPTION OF EXPERIMENTAL SYSTEM AND PROCEDURE

During the phase II SBIR² project CHA assembled and proved the utility of a 2.36-inch quartz-tube microwave reactor system for both NOx- and VOC-destruction studies. This unit, shown in Figure 1, was used to conduct the experimental work.

Figure 1. Microwave Reactor System for Design Optimization Studies



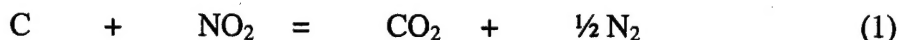
The system consists of a microwave generator, circulator, tuner, wave-guide, and a provision for cooling. Microwave power is generated from a Cober microwave generator that is adjustable between 0 and 6 kW at a fixed frequency of 2450 MHz. The load impedance of the reactor in the microwave field is matched to the generator impedance by adjusting the three-bolt tuner so that reflected power can be minimized and forward power maximized. The reactor is a 2.36-inch diameter quartz tube, 24 inches in length, located inside a 1/4-inch diameter copper helix, which serves as a non-resonant cavity. Two Hewlett-Packard power meters (Model 432A) were attached to a 60-dB directional coupler to monitor forward and reflected power. As the material in the reactor is heated, dielectric properties change, thus causing the impedance to change with time. The tuner is adjusted to compensate for this change. The reactor is packed with either char or catalyst and a mixed stream of vaporized N_2O_4 and nitrogen enters the reactor.

Because N_2O_4 disproportionates into NO_2 when vaporized, the N_2O_4 concentration was measured indirectly as NO_x by a chemiluminescence analyzer. At the low concentrations of our experiments, we were confident that interference by undissociated N_2O_4 would be insignificant. That measured removals converge on 100% appears to validate this assumption. To find the effectiveness of NO_x destruction by ethanol and reducing/oxidizing catalyst, ethanol was injected into a nitrogen stream containing NO_x . The mixture passed through a 12-inch catalyst bed in the 3.26-inch quartz tubular reactor. The injection rate of ethanol was 20% more than the stoichiometric equivalent. The superficial gas velocity used in these tests was 25 ft/min.

The reducing/oxidizing catalyst (Provoc-7, Pt/Rh catalyst) used for tests was purchased from Prototech Company (Boston, Massachusetts).

RESULTS AND DISCUSSION

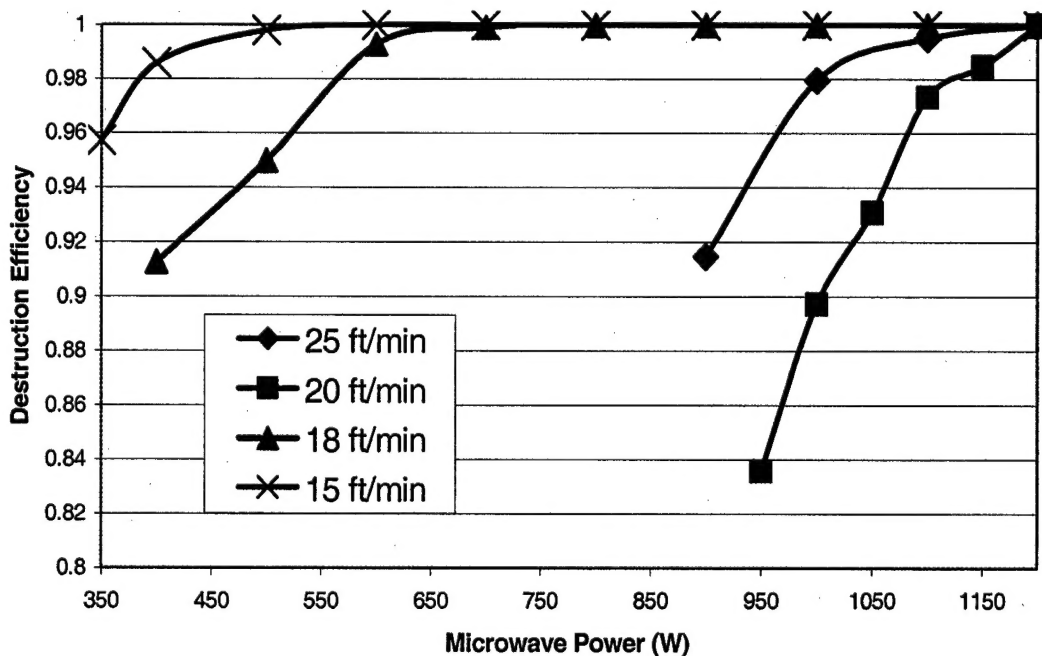
Nitrogen tetroxide (N_2O_4) decomposes quickly into nitrogen dioxide (NO_2) when mixed with a nitrogen stream. Also, a small fraction of NO_2 is decomposed into nitric oxide (NO) and oxygen. Pyrolytic carbon is an excellent reducing agent when exposed to microwave energy. When nitrogen dioxide contacts with pyrolytic carbon in microwave energy field, it reacts with carbon to produce nitrogen and carbon dioxide as follows:



Reaction (1) is favorable at low temperatures and reactions (2) and (3) become important at higher temperatures⁷. The microwave process for the treatment of oxidizer vapor consists of two microwave reactors (a carbon bed and an oxidation- catalyst bed). The carbon monoxide (CO) produced in the first carbon bed will be oxidized into carbon dioxide (CO_2) in the second microwave catalyst bed.

Destruction of N_2O_4 with char was tested using a 4-inch char bed in the 2.36-inch quartz tube reactor. The N_2O_4 flow rate was adjusted to maintain the inlet concentration at 5,000 ppm. Figure 2 presents the N_2O_4 destruction efficiency as a function of microwave power

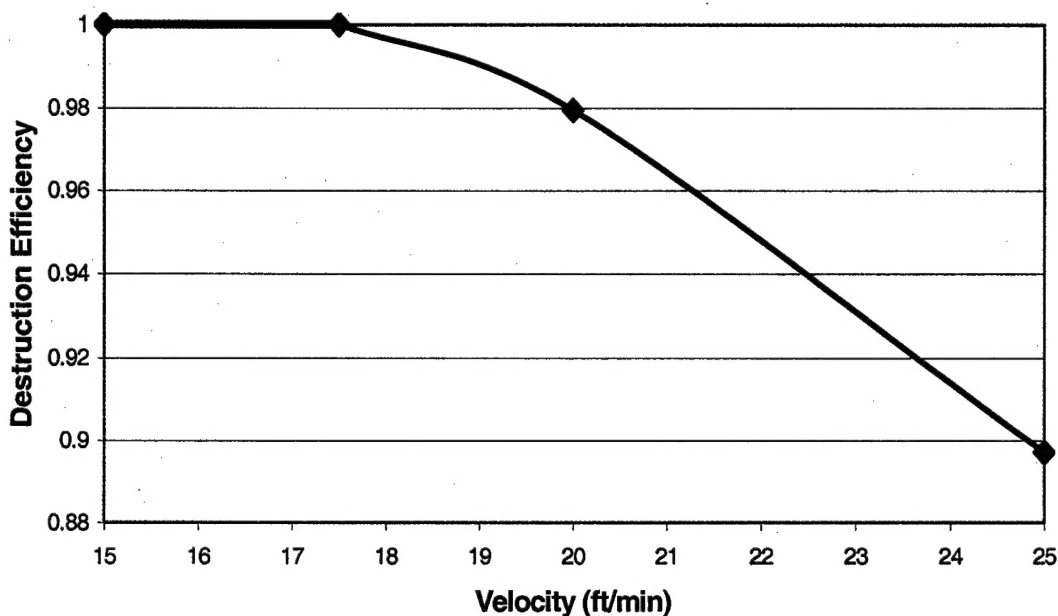
Figure 2. N_2O_4 Destruction Efficiency vs Microwave Power for 4-inch Char Bed



power at various superficial gas velocities. The N_2O_4 destruction efficiency was calculated using the concentrations of NO_x in the inlet and outlet nitrogen streams.

Data gathered from the destruction of N_2O_4 using char as the carbon reactant indicate that the reaction is controlled by the superficial gas velocity or the gas residence time in the char bed, as shown in Figure 2. Also, increasing microwave power increases the destruction efficiency as expected. Complete destruction of N_2O_4 was achieved with 500 W microwave power when the superficial gas velocity was 15 ft/min. When the superficial gas velocity for an empty bed increased to 25 ft/min, the microwave power required for the complete destruction of N_2O_4 was 1200 W. Figure 3 illustrates clearly the effect of the superficial gas velocity on the destruction of N_2O_4 .

Figure 3. N_2O_4 Destruction Efficiency vs. Superficial Gas Velocity at 1000 W Microwave Power in 4-inch Char Bed



To increase gas residence time, we increased the height of char bed to 8 inches. Figure 4 presents the N_2O_4 destruction efficiency as a function of microwave power at various superficial gas velocities. Figure 5 shows the N_2O_4 destruction efficiency as a function of the superficial gas velocity when 1 kW of microwave power was applied. Again destruction efficiency decreases as either the superficial gas velocity increases or microwave power decreases. However, the rate of decrease in destruction efficiency with increasing superficial gas velocity is lower for the 8-inch bed than for the 4-inch bed, as shown in Figure 6.

Figure 4. N_2O_4 Destruction Efficiency vs Microwave Input Power for 8-inch Char Bed

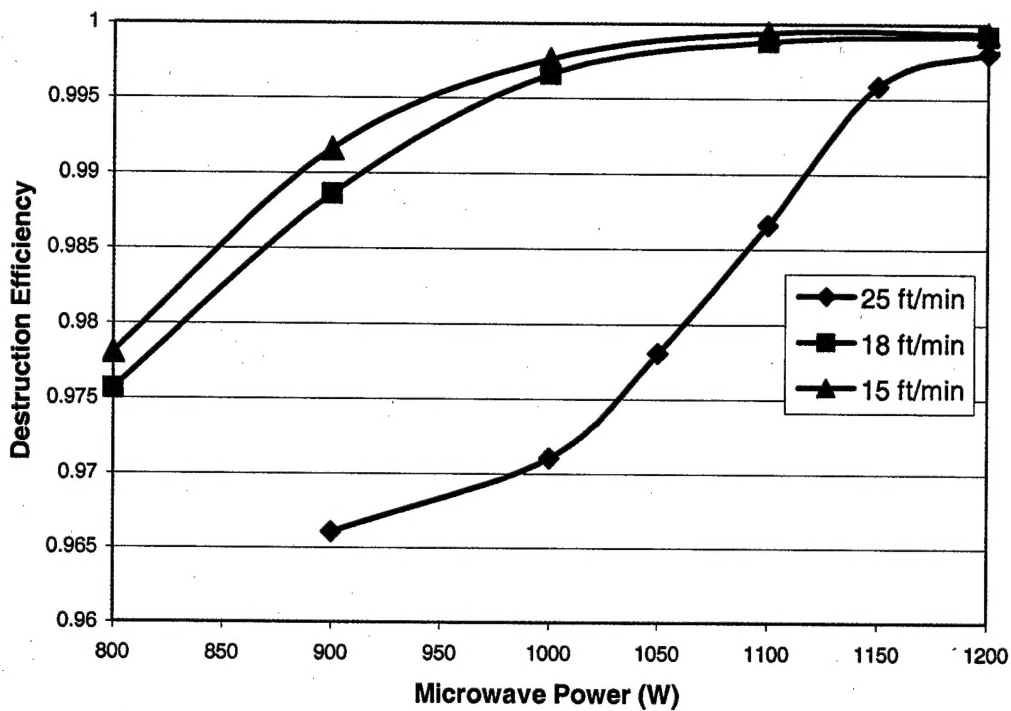


Figure 5. N_2O_4 Destruction Efficiency vs. Superficial Gas Velocity at 1000 W Microwave Power in 8-inch Char Bed

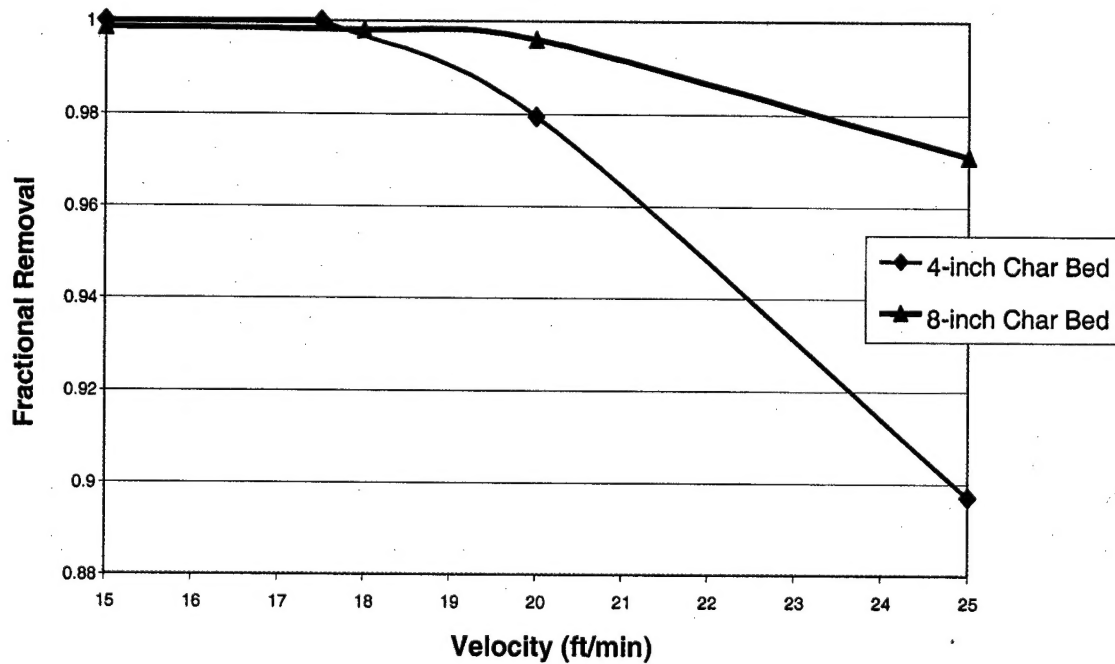
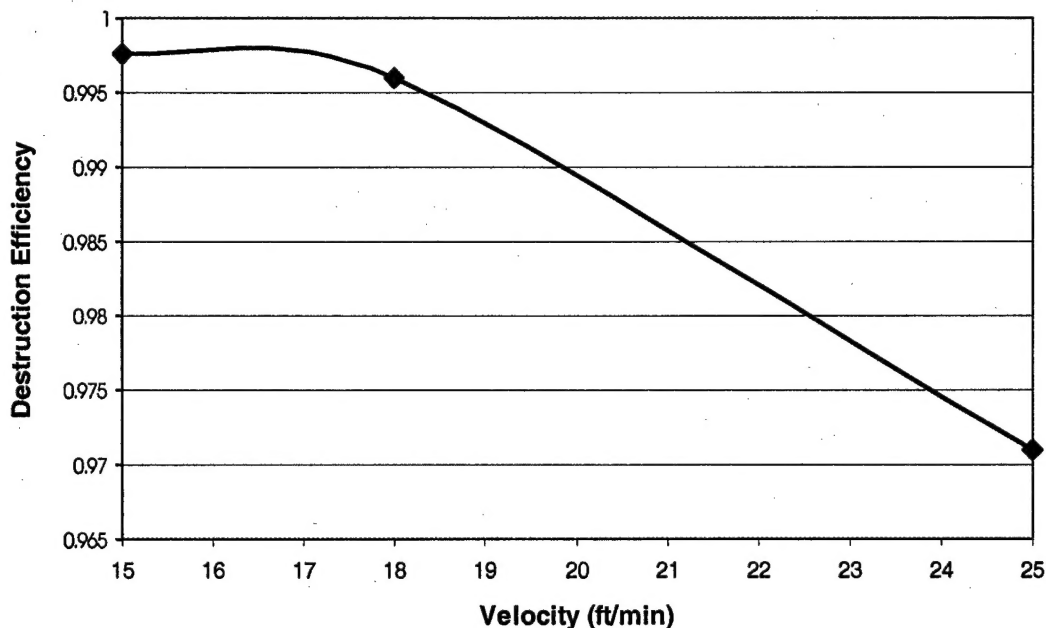


Figure 6. Comparison of 4-Inch Bed with 8-Inch Bed



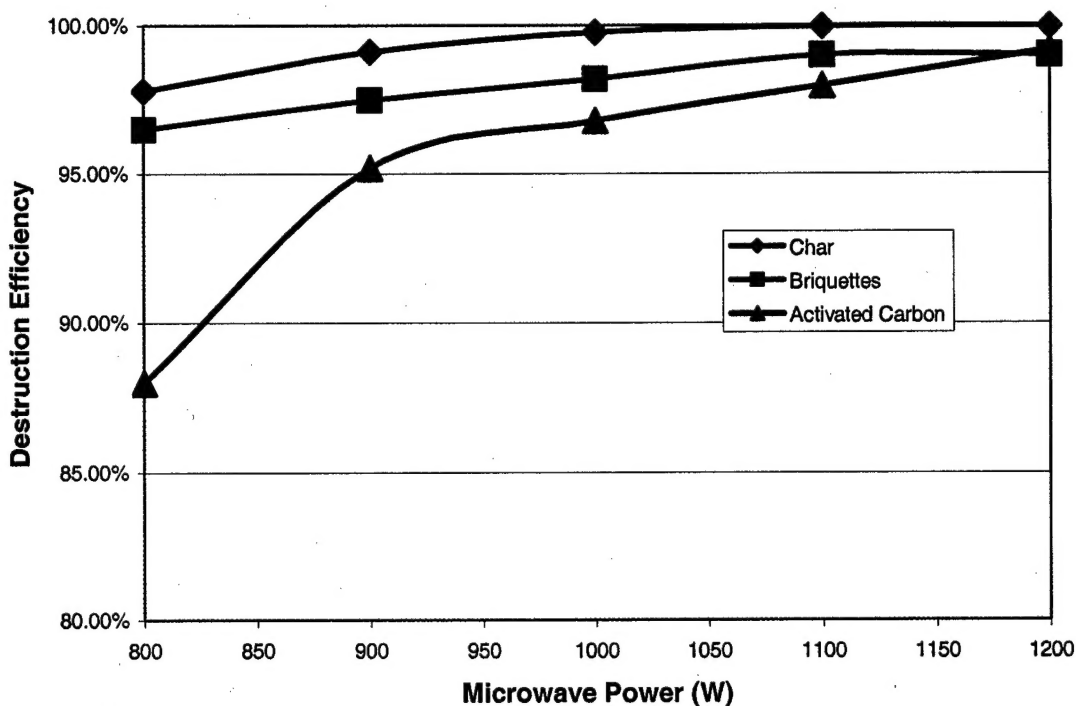
Three different pyrolytic carbons (char, form coke, and pelletized activated carbon) have been tested using a 6-inch carbon-bed and 25-ft/min superficial gas velocity.

Char and form coke are produced from subbituminous coal by ASTARIS Coke plant in Kemmerer, Wyoming. We have been using these pyrolytic carbons as reducing agents for microwave-induced decomposition of NO_x and SO_2 . Among these three pyrolytic carbons, char is the best reducing agent. However, form coke and pelletized activated carbons have stronger mechanical strength and would generate fewer fines. Pelletized activated carbon is more expensive but is a commercial product and easily available in the market. After test data on these carbons are obtained, we will select the best carbon for the microwave treatment of oxidizer vapors.

Figure 7 presents the destruction efficiencies of N_2O_4 for three different carbon reactants as a function of microwave power. As expected, char produced the best N_2O_4 destruction efficiencies at any given microwave power. The pelletized activated carbon gave the lowest destruction efficiencies, probably due to lower porosity caused by the binder used in the pelletizing process. However, all three carbon reactants provided excellent N_2O_4 destruction efficiencies.

The carbon reactant is consumed by reacting with NO_2 and needs to be resupplied. A continuous supply of carbon reactant will likely be inconvenient in a field operation. Since supplying a liquid reactant to the reactor is much easier than solid reactant, a new microwave processing method using ethanol and catalyst for the destruction of N_2O_4 was tested in the 2.36-inch reactor. Furthermore, a combination of carbon reactant and ethanol was also tested in the 2.36-inch reactor.

Figure 7. N₂O₄ Destruction Efficiency as a Function of Microwave Power for Three Carbon Reactants.



When a mixture of a reducing agent, *e.g.*, ethanol, and a nitrogen stream containing NO₂ (from dissociation of N₂O₄) passes through a reducing/oxidizing catalyst bed in a microwave energy field, NO₂ reacts with alcohol (reducing agent) as shown:

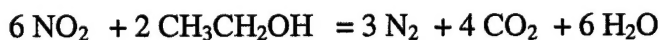
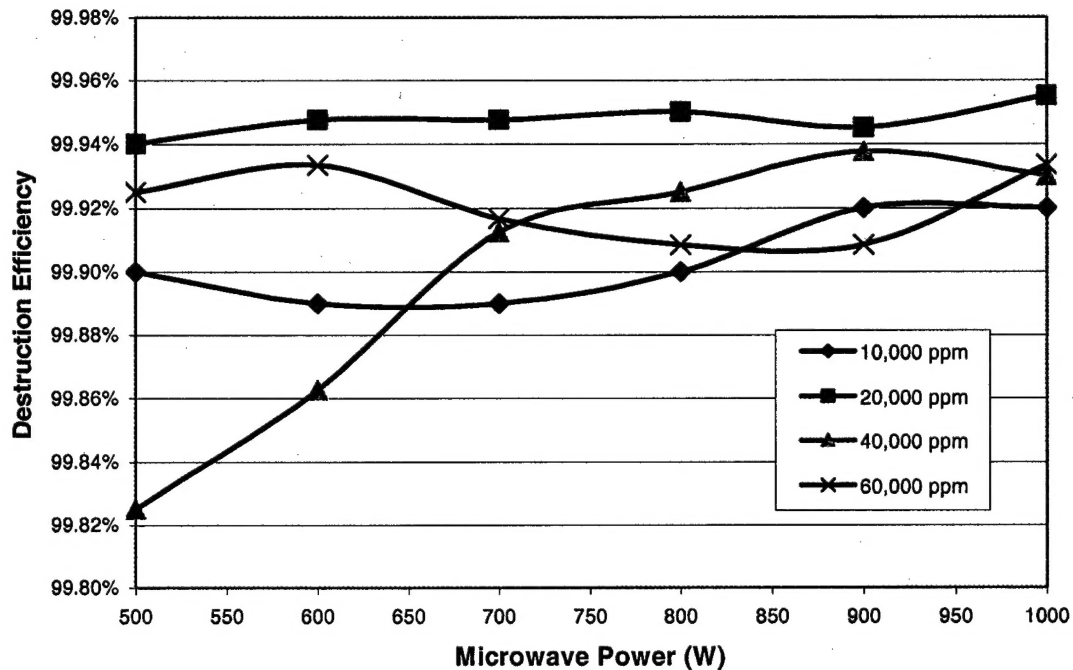


Figure 8 presents NO_x destruction efficiency as a function of microwave power for various concentrations of N₂O₄ in the inlet nitrogen stream. The N₂O₄ destruction efficiencies are greater than 99% for all test conditions used. Further, the N₂O₄ destruction efficiency is not dependent on the N₂O₄ inlet concentration. Figure 8 clearly demonstrates the advantage of using reducing agents and a reducing/oxidizing (three-way) catalyst for microwave destruction of N₂O₄.

An empty N₂O₄ tank contains a little N₂O₄ liquid as well as N₂O₄ vapors. Thus, the partial pressure of N₂O₄ in the vent gas from this tank will equal the vapor pressure of N₂O₄ at tank temperature. The inlet line to the NaOH scrubber has an orifice 0.344 inch in diameter to restrict gas flow into the scrubber. Total gas flow through the 0.344-inch orifice is ~36 scfm when the upstream pressure is 20 psig, dropping to ~5 scfm when the pressure is 3 psig. When the pressure is 20 psig, the mole fraction of NO_x in the nitrogen stream is 0.47 at 60 °F, and 0.58 at 70 °F. When the pressure is 3 psig, the mole fraction NO_x is 0.78 at 60 °F and 0.92 at 70 °F. Since the tank pressure decreases continuously,

Figure 8. N_2O_4 Destruction Efficiency vs Microwave Power Using Ethanol and Reducing /Oxidizing Catalyst

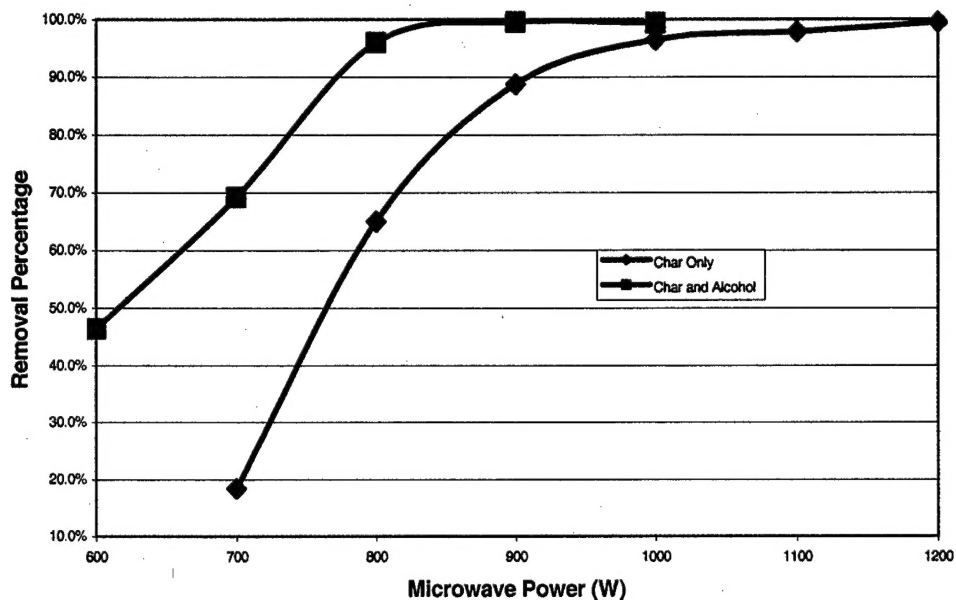


the gas flow rate and NO_x concentration continuously change during transfer operations. If ethanol is the only reductant used, the injection rate needs to be varied continuously to match changes in the N_2O_4 flow rate. A combination of a carbon reactant and ethanol may provide some advantages to maintain high N_2O_4 destruction efficiency.

A series of tests were conducted to find an improvement by adding ethanol to the carbon bed. An 8-inch char bed was prepared in the 2.36-inch quartz tube reactor for the test. The superficial gas velocity used for this series of tests was 25 ft/min. The N_2O_4 concentration in the inlet nitrogen stream was maintained at 5,000 ppm during the test. The experiment was run for approximately 30 minutes with char only and then ethanol was injected into the inlet nitrogen stream at 1 mL/min.

Figure 9 presents N_2O_4 destruction efficiency as a function of microwave power for the microwave destruction of N_2O_4 using char and ethanol. Data obtained from tests using only char are included in this figure for comparison. The addition of ethanol to the char bed improved the N_2O_4 destruction efficiency significantly as shown in Figure 9.

Figure 9. N_2O_4 Destruction Efficiency vs., Microwave Power for Tests Using Char and Ethanol



CONCLUSIONS

Phase 1 of the project to initiate practical implementation of the microwave destruction of oxidizer vapor has been completed. The main goal of Phase 1 was to develop a full-scale microwave reactor system for the destruction of oxidizer vapor (N_2O_4) and compare it to the current NASA packed-bed scrubber for managing the vapors. We completed design optimization experiments and tested a first-generation full-scale microwave reactor that is capable of treating 50–100 scfm of gas flow. We are also considering a prototype microwave system that utilizes a parallel set of 2.36-inch quartz reactors and is capable of treating 5–10 scfm for the field demonstration. The 2.36-inch quartz tube microwave reactor has performed well for the microwave destruction of toxic air pollutants.

It was also our goal to perform design optimization experiments to evaluate various carbon reactants including char, coke and activated carbon. New process concepts for the destruction of oxidizer vapor were also investigated. The following conclusions were drawn from the design optimization tests:

- Microwave power required for the complete destruction of oxidizer vapor increases as the superficial gas velocity increases.
- Increasing carbon bed height not only increases the N_2O_4 destruction efficiency but also reduces the rate of decrease in the N_2O_4 destruction efficiency as the superficial gas velocity increases.
- Among char, coke and pelletized activated carbon, char is the best carbon reactant for the microwave destruction of N_2O_4 .

- Ethanol reacts easily with N_2O_4 in nitrogen stream over the reducing/oxidizing catalyst by microwave energy and provides much greater destruction efficiency than carbon reactants.
- Addition of ethanol to the char bed improves the N_2O_4 destruction efficiency significantly at any given microwave power input.
- One kilowatt of power destroys approximately 0.4 pound of N_2O_4 .

KEYWORDS

Hydrazine; UDMH; nitrogen tetroxide; Titan; liquid fuel; air pollution; nitrogen oxides; microwave

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